January 1998 REAC 714

INSTRUCTOR'S INFORMATION

Studying S_N1 and S_N2 Reactions: Nucleophilic Substitution at Saturated Carbon

EQUIPMENT

General

aspirator
balance, 0.001-g
bottle, dropper
chips, boiling, acid-resistant
hood, fume

Product Characterization

Microboiling Point

apparatus, melting point
tubes, capillary, melting point

Density

microsyringe or pycnometer

Refractive Index

pipet, Pasteur, with latex bulb
refractometer

Infrared Spectroscopy

plates, KBr, NaCl, or AgCl
spectrophotometer, infrared

Individual

Microscale Synthesis

bath, sand*
2 beakers, 100-mL
clamp, utility
cylinder, graduated, 25-mL
flask, Erlenmeyer, 125-mL
6 pipets, Pasteur, with latex bulb
pipet, transfer, 1.0-mL
pipet, transfer, 2.0-mL
rod, stirring, glass
stand, support
test tube, 13 × 100-mm
test tube, 18 × 150-mm
tube, centrifuge, 15-mL
2 vials, 5-mL

Macroscale Synthesis

beaker, 50-mL
beaker, 400-mL[†]
2 clamps, utility
cylinder, graduated, 10-mL
glassware, standard taper:
  adapter, vacuum
  condenser, with tubing
  flask, round-bottom, 10-mL
  flask, round-bottom, 100-mL
  head, distilling
  thermometer, –10 to 260 °C, with adapter
heater, flask, 100-mL, with heat controller
2 pipets, Pasteur, with latex bulb
ring, support
2 stands, support
stopper, rubber, one-hole
test tube, 18 × 150-mm
tube, centrifuge, 15-mL
tubing, rubber
vial, product
Y-tube or T-tube[‡]

Rate Study

cylinder, graduated, 50-mL
cylinder, graduated, 100-mL
2 flasks, Erlenmeyer, 125-mL
micropipet, 50-µL
micropipet, 100-µL[§]
pen, marking
timer

* sand in crystallizing dish on electric hot plate or sand in electric heating well with heat controller

[†] for ice bath

[‡] for gas trap

[§] or adjustable micropipet set at 200µL

REAGENTS

(Required for 10 students. Reagent amounts include a 30% spillage allowance.)

Microscale Synthesis

13 g 1-butanol
5.2 g calcium chloride, anhydrous, granular
26 mL hydrobromic acid, 48%
13 mL sulfuric acid, concentrated
26 mL $NaHCO_3$, 5% aqueous
water, distilled or deionized

Macroscale Synthesis

65 g 1-butanol
13 g calcium chloride, anhydrous, granular
130 mL hydrobromic acid, 48%
ice
52 mL sulfuric acid, concentrated
65 mL $NaHCO_3$, 5% aqueous
water, distilled or deionized

Rate Study

0.65 mL 2-bromopropane
1950 mL 2-propanol
16 mL 0.5*M* NaOH
16 mL phenolphthalein
2.6 mL 2-bromo-2-methylpropane
0.65 mL 2-chloro-2-methylpropane
water, distilled or deionized

PREPARATIONS

1. 5% $NaHCO_3$ (100 mL): Dissolve 5 g $NaHCO_3$ in 95 g distilled or deionized water.

2. 0.5*M* NaOH (100 mL): Add distilled or deionized water to 4.0 g 50% NaOH to make 100 mL of solution. Alternatively, dissolve 2 g NaOH (MM: 40.00 g/mol) in distilled or deionized water to make 100 mL of solution.

3. Phenolphthalein solution (100 mL): Dissolve 0.5 g phenolphthalein in 50 mL ethanol*; then add distilled or deionized water to make 100 mL of solution. Place in a dropper bottle.

*absolute or 95%

CHEMICAL HANDLING

> ***Note:*** The information presented under **CHEMICAL HANDLING** may not conform to the latest Federal and state regulations because the regulations may have changed. Consult the appropriate agency for current information.
>
> Specific information listed here concerning each of the chemicals used in this experiment should be compared to the contents of the corresponding MSDS.

Spillage Cleanup (for ***small*** amounts of liquids or solids in the stockroom)

1. 2-Bromo-2-methylpropane: [***Caution:*** Flammable.] Mop up and prepare for incineration.

Or, use a spill kit to absorb the reagent and dispose of it by method recommended by local regulations.

2. 2-Bromopropane: [***Caution:*** Flammable.] See **1.** 2-Bromo-2-methylpropane.

3. 1-Butanol: [***Caution:*** Flammable.] See **1.** 2-Bromo-2-methylpropane.

4. Calcium chloride: Sweep up. Dissolve in water. Transfer to drain, diluting with a large amount of running water.

Or, dispose of by method recommended by local regulations.

5. 2-Chloro-2-methylpropane: [***Caution:*** Flammable.] See **1.** 2-Bromo-2-methylpropane.

6. Hydrobromic acid: [***Caution:*** Corrosive.] Neutralize with powdered $NaHCO_3$. Dilute with water. Mop up, transfer to drain, diluting with a large amount of running water.

Or, dispose of by method recommended by local regulations.

7. Phenolphthalein: Sweep up. Place in trash.

Or, dispose of by method recommended by local regulations.

8. 2-Propanol: [***Caution:*** Flammable.] Mop up and transfer to drain, diluting with a large amount of running water.

Or, prepare for incineration.

Or, use a spill kit to absorb the propanol and dispose of by method recommended by local regulations.

9. Sodium hydrogen carbonate: See **4.** Calcium chloride.

10. Sodium hydrogen carbonate, 5%: Mop up. Transfer to drain, diluting with a large amount of running water.

Or, dispose of by method recommended by local regulations.

11. Sodium hydroxide: [***Caution:*** Corrosive.] Sweep up. Transfer to an inert plastic container. Dissolve in *cold* water. Neutralize with 5% HCl. Transfer to drain, diluting with a large amount of running water.

Or, dispose of by method recommended by local regulations.

12. Sodium hydroxide, 0.5*M:* Neutralize with 5% HCl. Dilute with water. Mop up, transfer to drain, diluting with a large amount of running water.

Or, dispose of by method recommended by local regulations.

Collection Containers (for each work station servicing 10 students)

Containers, labeled as follows, should be available:

"Recovered Acid Layer" *
"Recovered Alcohol–Water Mixtures" [†]
"Recovered 1-Bromobutane"
"Recovered $CaCl_2$***"***
"Recovered Pot Residue" [‡]
"Recovered Washes"
"Used Pasteur Pipets"

*microscale
[†] rate study
[‡] macroscale

Disposal

1. Recovered acid layer: Dilute with water. Transfer neutralized solution to drain, diluting with a large amount of running water.

Or, dispose of by method recommended by local regulations.

2. Recovered alcohol–water mixtures: Transfer to drain, diluting with a large amount of running water.

Or, dispose of by method recommended by local regulations.

3. Recovered 1-bromobutane: [***Caution:*** Flammable.] Recover by drying and distilling.

Or, prepare for incineration.

Or, dispose of by method recommended by local regulations.

4. Recovered $CaCl_2$: Dissolve in water, transfer to drain, diluting with a large amount of running water.

Or, dispose of by method recommended by local regulations.

5. Recovered pot residue: [***Caution:*** Corrosive.] See **1.** Recovered acid layer.

6. Recovered Washes: See **2.** Recovered alcohol–water mixtures.

Hazard Alert

1. 1-Bromobutane [*Registry of Toxic Effects of Chemical Substances* ***(RTECS)***; 8 vols; U. S. Department of Health and Human Services, National Institute for Occupational Safety and Health, U. S. Government Printing Office: Washington, D. C., 1987, #EJ6225000]: Flammable and irritant. Fire hazard. Prevent eye, skin, and clothing contact. Avoid inhaling vapors and ingesting the compound.

2. 2-Bromopropane (***RTECS#*** TX4111000): Flammable and irritant. Fire hazard. Prevent eye, skin, and clothing contact. Avoid inhaling vapors and ingesting the compound.

3. 2-Bromo-2-methylpropane (***RTECS#*** TX4150000): Flammable. Fire hazard. Prevent eye, skin, and clothing contact. Avoid inhaling vapors and ingesting the compound.

4. 1-Butanol (***RTECS#*** EO1400000): Flammable and irritant. Fire hazard. Prevent eye, skin, and clothing contact. Avoid inhaling vapors and ingesting the compound.

5. Calcium chloride (***RTECS#*** EV9800000): Irritant and hygroscopic. Prevent eye, skin, and clothing contact. Avoid inhaling dust and ingesting the compound.

6. 2-Chloro-2-methylpropane (***RTECS#*** TX5040000): Flammable. Fire hazard. Prevent eye, skin, and clothing contact. Avoid inhaling vapors and ingesting the compound.

7. Ethanol (***RTECS#*** KQ6300000): Flammable and toxic. Fire hazard. Prevent eye, skin, and clothing contact. Avoid inhaling vapors and ingesting the compound.

8. Hydrobromic acid, 48% (***RTECS#*** MW3850000): Toxic and corrosive. Prevent eye, skin, and clothing contact. Avoid inhaling vapors and ingesting the compound.

9. Phenolphthalein (***RTECS#*** SM8380000): Irritant. Prevent eye, skin, and clothing contact. Avoid inhaling vapors and ingesting the compound.

10. 2-Propanol (***RTECS#*** NT8050000): Flammable and irritant. Fire hazard. Prevent eye, skin, and clothing contact. Avoid inhaling vapors and ingesting the compound.

11. Sodium hydrogen carbonate (***RTECS#*** VZ0950000): Moisture-sensitive. Prevent eye contact. Avoid inhaling dust.

12. Sodium hydroxide (***RTECS#*** WB4900000): Toxic and corrosive. Prevent eye, skin, and clothing contact. Avoid inhaling vapors and ingesting the compound.

13. Sulfuric acid, concentrated (***RTECS#*** WS5600000): Toxic and oxidizer. Prevent eye, skin, clothing, and combustible materials contact. Avoid inhaling vapors and ingesting the compound.

DEMONSTRATIONS

1. Demonstrate to students the techniques used to identify their reaction product: boiling point, density, and refractive index.

2. If students are unfamiliar with IR techniques, you may wish to demonstrate the methods they should use.

COMMENTS ON THE EXPERIMENT

Estimated bench time is 2.5–3 hr without the optional distillation.

1. It is assumed that S_N1 and S_N2 reactions have been discussed in lecture. The Background Information is intended as a review.

2. Students should be strongly warned regarding the corrosive power of concentrated H_2SO_4 and HBr. Should either of these two chemicals come in contact with a student's skin, the area should be rinsed immediately with running water. Small spills should be diluted with water and immediately neutralized with solid $NaHCO_3$.

3. You may wish to dispense acids using bottle-top dispensers, which dispense set liquid amounts.

4. The recommended gentle reflux is achieved in the microscale experiment by placing *only the very bottom* of the test tube in the sand bath and operating the heat control at a low setting.

5. A standard acid trap can be substituted in place of the Y-tube/aspirator described for Figure 7. Place a solution of 5% $NaHCO_3$ or 5% NaOH in a beaker. Extend rubber tubing from the top of the condenser to a funnel inverted over the top of the solution.

6. Have students note the densities of water, 1-bromobutane, and sulfuric acid. The 1-bromobutane product is the top layer in the reaction mixture, but 1-bromobutane is the bottom layer in all subsequent washings.

7. Drying the product with anhydrous $CaCl_2$ can be facilitated by shaking the test tube or by *warming* the solution cautiously in a sand bath.

8. The 1-bromobutane is sufficiently pure for characterization with no distillation. The final distillation may be omitted if time is a factor.

9. The final macroscale distillation of 1-bromobutane can be conducted using microscale glassware with elastomeric connectors.

10. Microscale product yields may not be sufficient to conduct *all* of the options under Characterizing the Product.

11. Students may work in groups of three to complete the section “Factors Affecting the Rates of S_N1 Reactions.” Each student would have responsibility for preparing the solutions for one of the three experiments. All students could then observe the reaction once the alkyl halides have been added and the reaction begun.

12. Accurate measurement of NaOH and alkyl halide volumes is *critical* to the success of the S_N1 rate study.

13. The study of solvent polarity may be extended to less polar solutions containing greater than 60% isopropanol. However, the alkyl halide is not completely soluble in solutions more polar than 40% isopropanol.

14. The test tube reflux microscale distillation is discussed in detail in Chemical Education Resource’s TECH 704, *Separating Cyclohexane and Toluene by Distillation*.

15. You may choose to photocopy the attached data sheet for student use.

REPRESENTATIVE STUDENT DATA

1. Student yields for the synthesis of 1-bromobutane range from 30–60%. The product is typically free of the 1-butanol starting material, and close agreement with accepted values for physical constants is obtained.

2. Reaction times for the S_N1 reactions should be approximately as follows:

Leaving group:	2-bromo-2-methylpropane	20 s
	2-chloro-2-methylpropane	2–3 min
Alkyl structure:	2-bromo-2-methylpropane	20 s
	2-bromopropane	> 1 week
Solvent polarity:	40% 2-propanol	15 s
	60% 2-propanol	40 s

Times may vary considerably, depending on the accuracy of measuring NaOH and alkyl halide volumes.

ANSWERS TO POST-LABORATORY QUESTIONS

1. Answers will vary. Percent yields should range between 30–60%. Because the scale is small, it is impossible to avoid loss of significant amounts of product by its adsorption on the glass surfaces of the containers.

2. Answers will vary. Students should compare measured values for physical constants with literature values for 1-bromobutane. This comparison is especially instructive if also made with literature values for 1-butanol. If an infrared spectrum is obtained, it should have no broad absorption band at 3500 cm^{-1}, characteristic of 1-butanol.

3. Under these conditions, 2-bromo-2-methylpropane reacts approximately 10 times faster than 2-chloro-2-methylpropane.

4. Bromide ion is a weaker base than Cl^- and, therefore, is a better leaving group. This difference is demonstrated by the relative rates of reaction of 2-bromo-2-methylpropane and 2-chloro-2-methylpropane.

5. Under these conditions, 2-bromo-2-methylpropane reacts well over 1000 times faster than does 2-bromopropane. The tertiary carbocation produced in the rate-determining step by 2-bromo-2-methylpropane is more stable and, therefore, is formed more rapidly. Consequently, the overall hydrolysis of 2-bromo-2-methylpropane occurs more rapidly than hydrolysis of 2-bromopropane.

6. The mixture containing 40% 2-propanol is more polar than the mixture containing 60% 2-propanol because water is more polar than 2-propanol.

7. The reaction occurs approximately 3 to 5 times faster in the more polar 40% 2-propanol mixture. A carbocation is formed in the rate-determining step of the S_N1 reaction. A more polar solvent solvates the carbocation, making it easier to form.

8. The structure of the alkyl group seems to have the greatest impact on reactivity in comparison to the other two variables.

ANSWERS TO PRE-LABORATORY ASSIGNMENT

1. Both H_2SO_4 and HBr are highly toxic. H_2SO_4 is oxidizing; HBr is corrosive.

2. The reaction site is generally less crowded for primary halides.

3. If the reflux is too vigorous, large amounts of HBr may be vaporized out of the test tube, thus reducing the yield of product.

4. As the reaction proceeds, the insoluble product forms a second layer in the reaction flask.

5. Anhydrous calcium chloride is used to remove water from the product.

6. BrBu = 1-bromobutane BuOH = 1-butanol

Microscale

$$\text{g BrBu} = 1.00\text{ g BuOH}\left(\frac{1\text{mol BuOH}}{74.1}\right)\left(\frac{137.0}{1\text{mol BrBu}}\right) = 1.85\text{ g}$$

Macroscale

$$\text{g BrBu} = 5.0\text{ g BuOH}\left(\frac{1\text{mol BuOH}}{74.1}\right)\left(\frac{137.0}{1\text{mol BrBu}}\right) = 9.2\text{ g}$$

7. As the S_N1 reaction occurs, H^+ ions are produced. These H^+ ions neutralize the OH^- ions originally present. When the pH of the solution becomes neutral, the indicator changes from its bright pink base form to its colorless acid form.

8. The time required for the indicator to change color is directly related to the amount of base added initially. The quantity of base must be measured accurately in order to achieve reproducible results.

9. HBr is a stronger acid than HCl. Therefore, Cl^- is a stronger base than Br^-.

name

section

date

Data Sheet

S_N2 Reaction

	g	*mol*
amount of 1-butanol used	___________	___________
amount of 1-bromobutane produced	___________	___________
product theoretical yield	___________	___________

product percent yield, % __________

Write the equation for reaction.

Product Characterization

	bp	*density*	*measured n_D*	*temp, °C*	*corrected n_D*
1-bromobutane					

S_N1 Reaction

	compound	*time*
Leaving group	2-bromo-2-methylpropane	
	2-chloro-2-methylpropane	
Alkyl structure	2-bromo-2-methylpropane	
	2-bromopropane	
Solvent polarity	40% 2-propanol	
	60% 2-propanol	